The Curvature of the Pressure–Temperature Relationship of a Pure Fluid on the Critical Isochore Very Near the Critical Point Under Gravity Influence

W. Wagner and N. Kurzeja
Lehrstuhl für Thermodynamik
Ruhr-Universität Bochum
D-44780 Bochum, Germany

Using a specially designed $p\rho T$ multi-cell apparatus in the immediate critical region of SF_6 and CO_2 we have found for all "thermal" critical exponents nearly "classical" values in the limiting approach to the critical point. Only at a certain distance from the critical point did we observe a transition to values which nearly meet the predictions of the renormalization group theory. Based on the corrections for the density stratifications this transition point could be identified as the limit of the gravity influence on the thermal behavior of SF_6 and CO_2, respectively. However, there are measurements of the isochoric heat capacity under zero gravity, which have yielded a non-classical value for the critical exponent α very close to the critical point. The only way to resolve this contradiction by direct thermal measurements seems to be the very careful examination of any deviation from the law of the rectilinear diameter for the phase boundary and the evaluation of the curvature of the *p-T* relationship on the critical isochore. According to existing theories both relationships should be correlated with the critical exponent α.

Since for the phase boundary we could not find any nonanalytical deviation from the law of the rectilinear diameter, we then focussed on extremely accurate and precise measurements of the absolute pressure on the critical isochore. As previous measurements could not reveal the rather weak curvature of the *p-T* relationship due to their restricted precision, we have therefore developed a rather sophisticated procedure to measure the absolute pressure on the critical isochore with an internal consistency unachievable up to now. Based on this high internal consistency of 1 ppm (in the case of SF_6) and 2 ppm (in the case of CO_2) of the absolute pressure for both regions above and below the critical point, we conclude that the thermal behavior of a pure fluid very close to the critical point ($\tau \leq 1\cdot10^{-4}$) can be represented very well by a linear function for $p(T)$. There seems to be no need for a second term with a value of the critical exponent α which differs from zero. Of course, greater temperature ranges can be better approximated with an additional second term, but the exponent of the second term shows a strong temperature dependence and has differed for both fluids.

Therefore, by very careful direct thermal measurements along the two possible evaluation paths of the critical exponent α, we cannot find any contradiction to our nearly classical results obtained for the critical exponents β, γ, and δ in the immediate vicinity of the critical point.